Laboratory Study on the Effects of Alkylation on Malaysian Coal for Coal Bed Methane Study

by

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13254

Final Draft Report submitted in partial fulfillment of

the requirement for the

Bachelor of Engineering (Hons)

Petroleum Engineering

MAY 2014

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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BACHELOR OF ENGINEERING (Hons)

(PETROLEUM)

Approved by,

_____

Dr. Saleem Qadir Tunio

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MUHAMMAD SYAFIQ BIN KAMARUL ZAMAN

ABSTRACT

Alternative energy source such as coal bed methane is gaining huge demand as the world's energy consumption is increasing every year. Coal bed methane gas is produced from coal seam reservoirs and often produced at shallow depths. Some of the gas is stored in the coal reservoir as free gas and some is held at the surface of the coal by adsorption in the micropores. The adsorbed gas can only be produce when the reservoir pressure is low. The complex structure of the coal makes it harder to produce the adsorbed gas because of the high pressure between the coal cleats. By changing the structure of the coal, the adsorbed gas will be release as free gas since the pressure between the coal cleats has been reduced. Alkylation of coal process is proved to increase the solubility of coal by changing the structure of the coal using alkyl halides. There are many type of alkylation agent for the alkylation process and the quality of the product is depending on them. In this study, the effect of alkylation on the characterization of the coal is determined. The coal sample is first subjected to alkylation process using two different alkylating agents (a straight chain and a branched chain alkylating agents) by refluxing the coal sample with the alkylating agent for 24 hours. It is found that the alkylation process increases the weight of the coal sample by 21.54% when a branched chain alkylating agent is used and only 13.88% when a straight chain alkylating agent is used instead. Apart from alkylating the coal, the characterization using the Fourier Transform Infrared spectroscopy is performed to identify the molecules that are present in the coal. The branched chain alkylating agent gave more infrared absorption peaks as compare to the straight chain alkylating agent. Therefore, a branched and longer carbon chain of alkylating agent used for the alkylation process has more effect on the coal.

ACKNOWLEDGEMENT

First and foremost, I give my highest gratitude to Universiti Teknologi PETRONAS (UTP) for the chance of conducting this research for the completion of my degree as well as for future work life preparation.

I am grateful to my supervisor, Dr. Saleem Qadir Tunio for his assistance and guidance throughout the project. I am thankful to Ms. Noor Ilyana Binti Ismail and Mr. Muhammad Aslam B Md Yusof, the coordinators of Final Year Project (FYP) for their attention and support during the completion of this project.

I would like to dedicate my gratitude toward my mother, Prof. Madya Zuraidah Binti Abdullah Munir and also Prof. Madya Dr. Zurina Binti Haji Shaameri, lecturers of Universiti Teknologi MARA (UiTM) for helping and allowing me to perform part of the project at their laboratory.

My appreciation also goes to all the research officers, lab technicians, seniors, family members and friends for their help and support whether directly or indirectly to this project.

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NOMENCLATURE

θ	Number of active sites of the surface of adsorbent that undergoing adsorption
λ	Wavelength
$=CH_2$	Methylene
A	Adsorbate
$AlCl_3$	Aluminum chloride
B	Adsorbent
Br	Bromine
C	Ratio of equilibrium constant when single molecule adsorbed per vacant site over the equilibrium constant to the saturated vapor liquid equilibrium
c	Speed of light
C_2H_5I	Ethyl iodide
C_3H_8Cl	Propyl chloride
C-H	Carbon hydrogen bond
C=C	Carbon double bond
CBM	Coal Bed Methane
CH_3	Methyl
Cl	Chlorine
CO_2	Carbon dioxide
F	Fluorine

FTIR	Fourier Transform Infrared
H_2	Hydrogen gas
HCl	Hydrochloric acid
I	Iodine
IR	Infrared
K	Equilibrium constant for distribution of adsorbate between the surface and gas phase
k	Adsorbent specific temperature
m	Unit mass of solid adsorbent
N_2	Nitrogen
n	Gas specific temperature
nK	Metallic potassium
O-H	Hydrogen bond
P	Pressure
P_s	Saturation pressure
RCl	Alkyl chloride
THF	Tetrahydrofuran
v	frequency
V_{mono}	Adsorbed volume of gas at high temperature condition
W	Wavenumber
x	Unit mass of gas

CHAPTER 1

INTRODUCTION

1.1 Background

Coal bed methane is a natural gas produced from coal beds and is formed by the geological process of coal generation [1]. Figure 1.1 shows coal bed methane is produced at shallow depths and it is produced with large amount of water [2]. For coal bed methane well, the water production comes in large volumes at the early stages of the production [3, 4, 5]. As the amount of water inside the coal decrease, the amount of methane production starts to increase [3, 4, 5]. More than ninety percent of the gas is methane and the remaining is a very small proportion of heavier hydrocarbons such as ethane and butane as well as other gases such as carbon dioxide and hydrogen sulfide [1]. Coal bed methane is important for the industries since it is an alternative energy source to support the increasing demand for energy [2, 6].

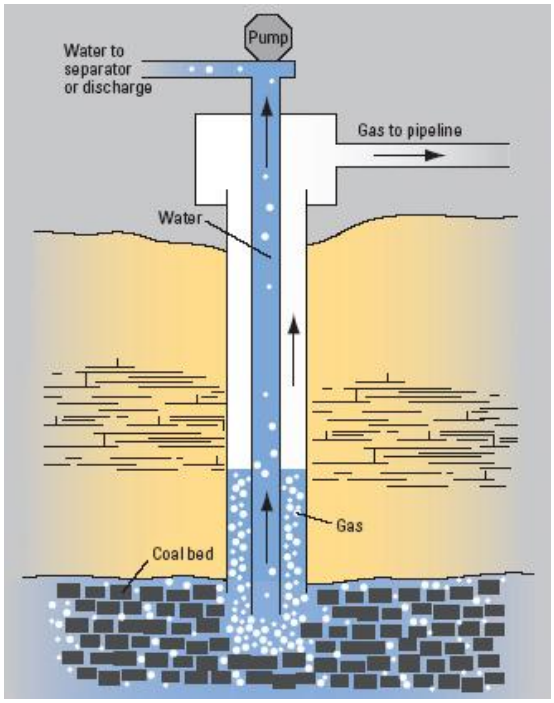


Figure 1.1: Schematic diagram of a coal bed methane well. [7]

Coal bed methane can be recovered by two methods, which are primary recovery and enhanced coal bed methane recovery [2]. The primary method can recover coal bed methane up to 60% of the reserve and the enhanced coal bed methane method can recover up to 80% of the reserve [2]. For enhanced coal bed methane recovery, gases such as carbon dioxide and nitrogen are injected into the coal seams to displace the methane that has been adsorbed on the surface of the coal to improve the recovery of methane from the reservoir [8, 9].

On the other hand, coal is a type of sedimentary rock that is formed by the burial of dead plant with sediments under high temperature and pressure [10]. There are four ranks of coal that have been classified as a result of the variation of materials that was buried with the dead plant as well as the time factor for the coal to form [11, 12]. The four ranks of coal in are Lignite, Sub-bituminous, Bituminous and Anthracite and the rank is increasing from Lignite to Anthracite [11, 12, 13, 14]. The energy content of the coal is higher as the rank of coal increases since it has more carbon content [13, 14, 15].

Coal can react with many substances and undergoes different processes such as combustion, hydrogenation, halogenation, hydrolysis and alkylation. Alkylation of coal is a process that increases the solubility of the coal in various organic solvents and hence enhancing its reactivity to liquefaction. Coal allows itself to be alkylated by substituting one of its hydrogen atom with an alkyl group. [18]

Therefore, this project will study the effects of alkylation on the characterization of Malaysian coal by reacting coal with alkyl halides.

1.2 Problem Statement

Coal bed methane is a natural gas produced from coal bed and is formed by the geological process of coal generation. Some of the gas is stored in the coal reservoir as free gas and some is held at the surface of the coal by adsorption in the micropores. The adsorbed gas can only be produce when the reservoir pressure is low. The complex structure of the coal makes it harder to produce the adsorbed gas because of the high pressure between the coal cleats. By changing the structure of the coal, the adsorbed gas will be release as free gas since the pressure between the coal cleats has been reduced.

Alkylation of coal process is proved to increase the solubility of coal by changing the structure of the coal using alkyl halides. There are many type of alkylation agent for the process and the quality of the product is depending on them. Therefore, a study to identify which alkylating agent will have more effects on the properties of the product that can affect the methane adsorption of the Malaysian coal should be conducted.

1.3 Objectives

The objectives are to:

- Determine the porosity and permeability of Malaysian coal sample before alkylation process.
- Characterize the coal sample and its alkylated products.

1.4 Scope of Study

The scopes of study for this project are:

- Type of alkylation process.
- Components of alkylation process.
- Characterization of coal.

CHAPTER 2

LITERATURE REVIEW

2.1 General Description of Coal

Coal is a type of sedimentary rock that is formed by the burial of dead plant with sediments under high temperature and pressure [10]. Dead plant started to decay when they fell to ground and new plants grew over the decaying plant [11]. The layer of the decaying vegetation was pressed tightly together by the material on top of it and over a long period of time, pressure turned the vegetation into peat [11]. This process was repeated for several times until the peat turned into coal as water was squashed out of the peat [11].

There are four ranks of coal that have been classified as a result of the variation of materials that was buried with the dead plant as well as the time factor for the coal to form [11, 12]. The four ranks of coal in are Lignite, Sub-bituminous, Bituminous and Anthracite and the rank is increasing from Lignite to Anthracite [11, 12, 13, 14]. Different ranks of coal have different carbon content, volatile matter and moisture content as shown in Table 2.1 [11, 13, 14, 15]. Generally, higher rank of coal has higher carbon content and it has lower volatile matter and moisture content compared to lower rank of coal [14, 15]. The detail for each rank of coal is shown in Table 1 below [15].

Table 2.1: Detail for each rank of coal. [15]

Rank of Coal	Carbon Content (%)	Volatile Matter (%)	Calorific Value (kJ/kg)	Moisture Content (%)
Peat	60	> 53	16800	> 75
Lignite	60 – 71	49 – 53	23000	35
Sub-bituminous Coal	71 – 77	42 – 49	29300	10 – 25
Bituminous Coal	77 – 87	29 – 42	36250	8
Anthracite	> 87	8 – 29	> 36250	< 8

More than 70 % of the coal's volume is made of carbon and this value is depends on the rank of the coal [14]. Higher rank of coal has higher carbon content since it contain less hydrogen, oxygen and nitrogen [14]. Higher carbon content leads to a higher calorific or energy value because it gives off more heat during combustion [14, 15].

Volatile matter is the material that is produced from the coal when it is heated to 950°C in the absence of air under specific conditions [14]. The components of coal, such as carbon, hydrogen, oxygen and sulfur is liberated usually as a mixture of short & long chain hydrocarbons, aromatic hydrocarbon and some sulfur [14, 16]. The volatile matter is consists of a mixture of gasses, organic compounds and tars [14]. As the rank of coal increases, the volatile matter becomes lesser [14].

Moisture is an important property of coal as it is necessary for burning coal to have low water content. As the rank of coal increases, the moisture content decreases. Groundwater and other extraneous moisture make the coal wet and it can be readily evaporated at room temperature. This type of moisture is called the adventitious moisture. The inherent moisture is the moisture held within the coal itself and it is difficult to be removed. There are four possible forms of moisture in coal, which are surface, hydroscopic, decomposition and mineral moisture. The water held on the surface of coal particle or macerals is called the surface moisture. Hydroscopic moisture is for the water held by capillary action within the microfractures of coal. The water held within the coal's decomposed organic compounds is called the decomposition moisture and the mineral moisture is the water which comprises part of the crystal structure of hydrous silicates, such as clays minerals. Moisture is determined by the total moisture that is calculated as the weight loss between the untreated and analyzed samples. For low-rank coals, the moisture can be determined by heating the coal with toluene or by drying the coal in minimum free-space oven at 150°C in nitrogen atmosphere and for high-rank coals, the moisture can be determined by drying the coal in air at 100°C to 105°C. The method for the high-rank coals can also be used to determine the inherent moisture when in vacuum condition but it is not suitable for the low-rank coals because oxidation may take place. [17]

2.2 Alkylation of Coal

Alkylation is a process of transferring an alkyl group into a molecule from other molecule. This process will significantly change the properties of the molecule and allow for numerous commercial processes to take place. For example, the reaction of isobutene with propene or butene in the presence of a catalyst will produce isoparaffins for high quality motor fuel. [19, 20]

Alkylation of coal is a process that increases the solubility of the coal in various organic solvents and hence enhancing its reactivity to liquefaction. Coal allows itself to be alkylated by substituting one of its hydrogen atom with an alkyl group. Figure 2.1 shows an example of the process is reacting alkyl chloride with coal in the presence of aluminum chloride in a solvent such as carbon disulfide. The reaction increases the solubility of the coal from 11% to 39% pyridine-soluble material. Another example of alkylation of coal is reacting coal with alkene or alcohols in the presence of aluminum chloride will increase the solubility of the coal to more than 50% in quinoline solution. [18]

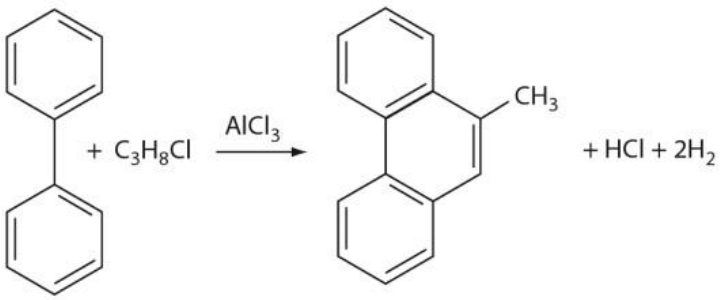


Figure 2.1: Chemical reaction of coal and alkyl chloride in the presence of aluminum chloride. [18]

Reductive alkylation was introduced as the alkylation of coal concept expanded to numerous studies relating to the coal structure [18, 21, 22, 23, 24]. It is necessary to reacts the coal with metallic potassium and naphthalene in tetrahydrofuran [18]. Below

is the chemical reaction for the reductive alkylation of coal by using metallic potassium and naphthalene in tetrahydrofuran [18].

$$\text{Coal} + n\text{K (in THF/naphthalene)} \rightarrow \text{Coal}^{n-}\ n\text{K}^{+} \qquad [18]$$

'Coal anion' is produced as the product of the reaction through an electron transfer process and then it can be alkylated by using alkyl iodide. Below is the chemical reaction for the alkylation process. [18, 22, 23, 24]

$$\text{Coal}^{n-} + n\text{C}_2\text{H}_5\text{I} \rightarrow \text{coal}(\text{C}_2\text{H}_5) + n\text{I}^{-} \qquad [18, 22, 23, 24]$$

In 1877, Charles Friedel and James Crafts discovered two reactions to attach molecule to an aromatic ring [25]. One of the reactions is called Friedel-Crafts alkylation that uses alkyl halide to alkylate an aromatic in the presence of strong Lewis acid catalyst [25]. This reaction is applicable to alkylate coal since coal is a complex macromolecule and mostly consist of aromatic structure [18, 26]. Figure 2.2 shows a coal consists of a number of benzene rings is react with alkyl halide such as alkyl chloride in the presence of strong Lewis acid catalyst such as aluminum chloride will substitute one of it hydrogen atom with the alkyl molecule from the alkyl chloride [25].

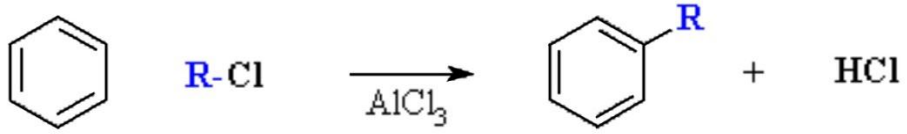


Figure 2.2: Chemical reaction of Friedel-Crafts alkylation of a benzene ring with alkyl chloride in the presence of aluminum chloride. [25]

There are three components for the alkylation process of a coal which are the type of solvent, the type of alkylating agent and the presence of a catalyst. Solvents such as carbon disulfide, pyridine, quinolone, liquid paraffin, anthracene oil and tetralin have different rate of effectiveness in term of the extractability of the product for the alkylation process. Anthracene oil proved to be the best solvent for the process while tetralin gave poor result. Alkylating agents such as alkyl halides, alkanes, alkenes and alcohols are also have some effects to the extractability of the product. The use of aluminum chloride as a catalyst improves the extractability of the product by a good amount. [26]

2.3 Comparison between Conventional Gas and Coal Bed Methane

Natural gas consists primarily of methane and it is produced from both conventional and unconventional reservoirs. It is easier to produce from the conventional reservoir than the unconventional reservoir. The major differences between the conventional and unconventional natural gas are the method, difficulty and cost to produce the gas. [27]

Conventional gas is occupying the pore spaces of the rock formation as free gas [27]. The gas is trapped in the rock structures that are caused by folding or faulting of sediment layers [28]. Some factors are required for the conventional gas to be accumulated [28]. The factors are source rock, migration, trap and reservoir [28]. Source rock is an organic rock that produces the hydrocarbons [28]. It composed of either marine or terrestrial organic debris that has been compacted by layers of rocks at high pressure and temperature [28]. Channels of interconnected pore spaces of the rock allow the hydrocarbon produced by the source rocks to migrate upwards due to the pressure of the reservoir until they reach the trap [28]. Trap or seal is a non-porous or impermeable layer of rock that restricts the flow of fluid [28]. It allows the accumulation of hydrocarbons into a certain location inside the formation [28]. The high porosity and permeability rock that holds the hydrocarbons below the trap is called the reservoir [28].

Coal formations are both the source rock and the reservoir for the coal bed methane [5]. Methane is held at the surface of the coal by adsorption in the micropores [3, 5, 33, 34]. The gas is produced by reducing the reservoir pressure during the coal bed methane production [3, 4, 5]. Reducing the reservoir pressure can be achieved by dewatering the reservoir [3, 4, 5]. Therefore, water must be removed before methane can be produced in the early production life of a well [3, 4, 5]. During the early stage of the production, only small volume of methane can be produced as shown in Figure 2.3 [3, 4, 5]. When pressure has decreased sufficiently by removing the water, only then the methane production will increase [3, 4, 5]. Figure below shows the relationship between the water and methane production over the time of the production [29].

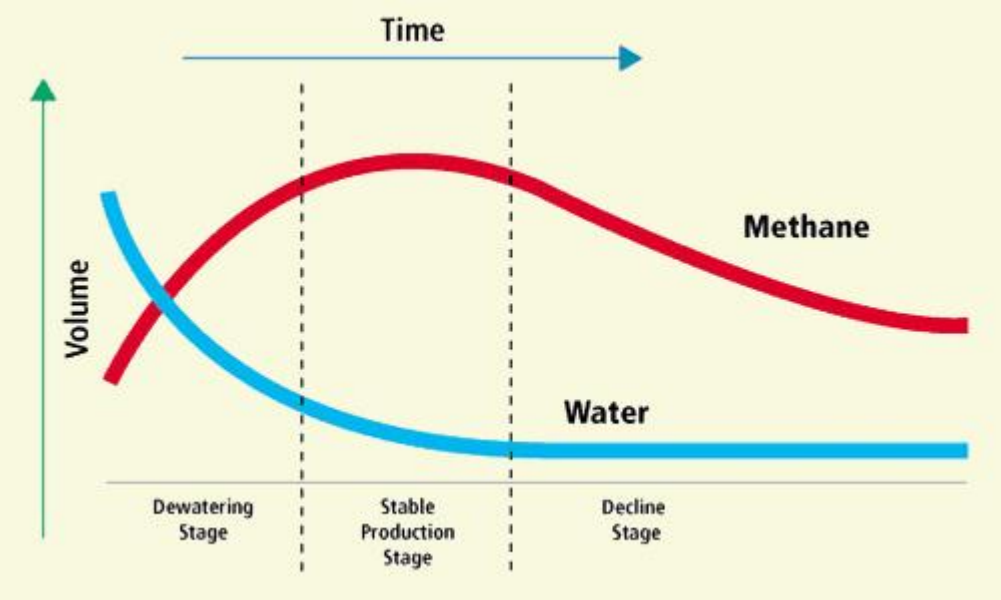


Figure 2.3: The relationship between water and methane production over the time of production. [29]

Some of the coal bed methane is stored in the coal reservoir as free gas and some is held at the surface of the coal by adsorption in the micropores [3, 5, 33, 34]. The adsorbed gas is stored differently than the free gas and its adsorption nature is described by the gas adsorption theory [33].

2.4 Coal Adsorption

Coal adsorption is a mechanism for hydrocarbon gases to be stored in a coal reservoir [3]. It is not the same as the mechanism of gas storage in the conventional reservoir [3, 33, 34]. Hydrocarbon gases are occupying the pore spaces in conventional reservoir as free gas, however for a coal reservoir, methane is held to the surface of the coal by adsorption in the micropores [3, 5, 33, 34]. Large volume of gas is able to be stored in the coal since the surface area within the micropores is very large [3]. For example, one pound, of coal has a surface area of 55 football fields and one ton of coal has a surface area of one billion square foot [3]. The gas in a good coal bed well in San Juan or Warrior Basin would have two or three times more volume than a sandstone reservoir of identical depth having 25% porosity and 30% water saturation [3].

For the conventional reservoir, the gas is stored by the principle of the gas laws since it is affected by the pressure, volume and temperature of the reservoir [33]. However, the adsorbed gas in the coal reservoir is not affected by the gas laws and it takes up significantly less space than the gas of the same mass would require within the pore spaces of the conventional reservoir [33]. Langmuir Isotherm is used to determine the quantity of the adsorbed gas in coal reservoir at constant temperature [33]. Most of the parameters used in the Langmuir Isotherm are required during coring, logging and drilling operation [33]. The term “Isotherm” refers to the volume of gas adsorbed on the surface of a solid as the function of pressure for a specific temperature, gas and solid material [35]. According to Type I Adsorption Isotherm, the amount of adsorbed gas in a microporous solid is asymptotic with pressure as the pressure is increases and the amount of adsorbed gas is decreases as the temperature is increases [35].

In order for the adsorbed gas to be released or produced, the pressure in the matrix of the coal need to be reduces. Therefore, water must be removed before methane can be produced in the early production life of a well. [3, 4, 5]

2.5 Adsorption Isotherms

The process of adsorption data is usually represented by an adsorption isotherm which is a plot of the quantity of absorbate adsorbed on the surface of adsorbent against the pressure at constant temperature [30, 31]. The adsorbate is adsorbed on the adsorbent is the basic of adsorption isotherm [30]. Furthermore, there are three different theories in adsorption isotherms that are commonly used to study the adsorption process [30]. The theories in adsorption isotherms are Freundlich, Langmuir and BET theory [30]. Below is the reaction process between the adsorbate and the adsorbent [30]. AB is the product of the adsorption process [30].

$$A + B \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB \qquad [30]$$

Freundlich Isotherm is an empirical expression that represents the adsorption of a unit mass of gas adsorbed by a unit mass of a solid adsorbent as a function of pressure at constant temperature. The Freundlich Isotherm is applicable for the relationship of adsorption with pressure at low pressure condition. Below is the equation of the Freundlich Isotherm. [30]

$$\frac{x}{m} = kP^{\frac{1}{n}} \qquad [30]$$

Langmuir Isotherm states that dynamic equilibrium exists between the adsorbed gaseous molecules and the free gaseous molecules. It is the relationship between the numbers of active sites of the surface of adsorbent that undergoing adsorption as a function of pressure. The Langmuir Isotherm is limited only for low pressure condition. Below is the equation for the Langmuir Isotherm. [30]

$$\theta = \frac{KP}{1 + KP} \qquad [30]$$

BET Theory states that multilayer formation is the actual case of adsorption. Monolayer in nature is one of the assumptions of Langmuir Isotherm. At low pressure condition, gaseous molecules have high thermal energy and escape velocity. As a result, few numbers of gaseous molecules are available near the surface of the adsorbent. At high pressure and low temperature condition, the gaseous molecules have low thermal energy. Therefore, more gaseous molecules are available near the surface of the adsorbent. Under this condition, multilayer adsorption occurs and it is explained by the BET Theory. Below is the BET equation. [30]

$$V_{total} = \frac{V_{mono} C \left(\frac{P}{P_o}\right)}{\left(1 - \frac{P}{P_o}\right)\left[1 + C\left(\frac{P}{P_o}\right) - \frac{P}{P_o}\right]} \qquad [30]$$

There are five different types of adsorption isotherm, which are the Type I, Type II, Type III, Type IV and Type V Adsorption Isotherm. Figure 2.4 shows Type I Adsorption Isotherm that represents the monolayer adsorption and it can be easily explained by using the Langmuir Isotherm. The example for Type I Adsorption Isotherm is the adsorption of oxygen on carbon black at 183°C. [30, 32]

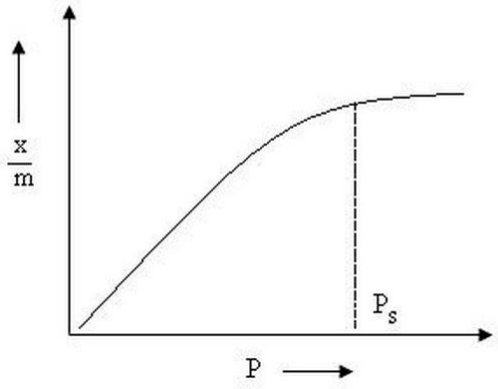


Figure 2.4: Type I Adsorption Isotherm. [30]

Type II Adsorption Isotherm shows large deviation from the Langmuir Isotherm. The middle flat region in the isotherm is corresponding to the monolayer formation as shown in Figure 2.5 [30, 32]. The example for this type is the adsorption of water vapour on carbon black at 30°C [32].

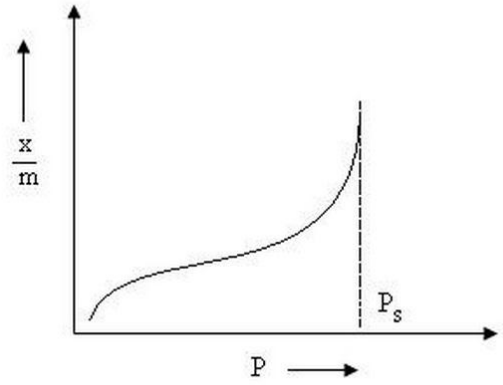


Figure 2.5: Type II Adsorption Isotherm. [30]

Figure 2.6 shows Type III Adsorption Isotherm describes the formation of multilayer and there is no flat region in the isotherm which indicates that the absent of the monolayer [30]. The example for Type III Adsorption Isotherm is the adsorption of Bromine or Iodine on silica gel at 20°C [32].

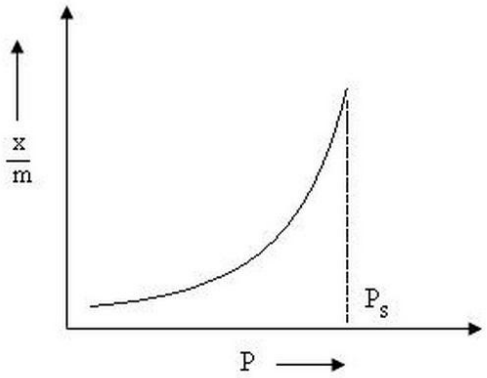


Figure 2.6: Type III Adsorption Isotherm. [30]

For Type IV Adsorption Isotherm, formation of monolayer is followed by multilayer as shown in Figure 2.7. There is a possibility of gases to be condensed in the tiny capillary pores of the adsorbent at pressure below the saturation pressure of the gas. The example for this type is the adsorption of Benzene on Iron Oxide or silica gel at 500°C. [30]

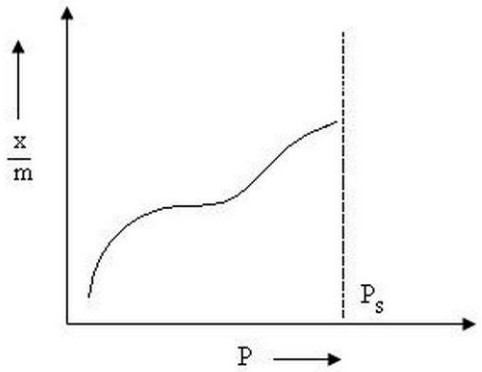


Figure 2.7: Type IV Adsorption Isotherm. [30]

Figure 2.8 shows Type V Adsorption Isotherm which also describes the phenomenon of capillary condensation of gas similar to Type IV Adsorption Isotherm. Adsorption of water vapors at 1000°C on charcoal is the example for this type. Below is the figure for Type V Adsorption Isotherm. [30]

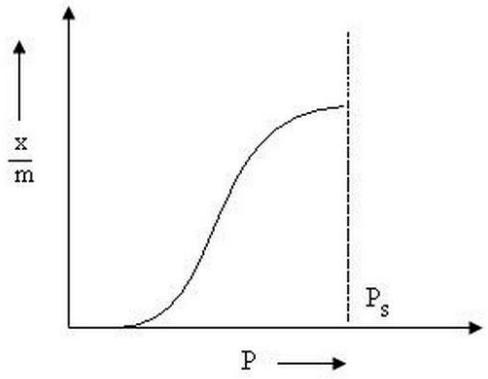


Figure 2.8: Type V Adsorption Isotherm. [30]

2.6 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy studies the interaction of infrared light with matter [36]. It identifies chemical compounds in paints, coatings, polymers, medicines, foods and other products [37]. The Fourier Transform Infrared Spectroscopy provides quantitative and qualitative analysis for organic and inorganic samples [37]. It is an effective analytical instrument for characterizing covalent bonding and detecting functional groups [37]. Fourier Transform Infrared Spectroscopy identifies chemical bonds in a molecule by producing an infrared absorption spectrum, which is the fundamental measurement that plots the measured infrared intensity versus the wavelength or the frequency of light [36, 37].

Infrared radiation is passed through a substance in Infrared Spectroscopy. Some of the infrared radiation is absorbed by the substance and the remaining infrared radiation passed through. The molecular fingerprint of the substance is created as the resulting spectrum represents the molecular absorption and transmission. Like human fingerprint, different substance or material has a unique combination of atoms. Therefore, no two compounds can produce the same infrared spectrum. [38]

In Infrared Spectroscopy, units called wavenumbers are commonly used to indicate different types of light [36]. The relationship of speed of light, frequency and wavelength is shown in the following equation:

$$c = v\lambda \qquad [36]$$

The equation below shows the relationship of wavelength and wavenumber of light:

$$W = 1/\lambda \qquad [36]$$

These equations show that light waves can be described by their frequency, wavelength and wavenumber. Usually, light waves are referred by their frequency or wavelength but their wavenumber is used for the infrared absorption spectrum instead as shown in Table 2.2. [36]

Table 2.2: Wavenumber of several types of light. [36]

> 14000 cm^{-1} Visible UV & X-rays	14000 cm-1 Near Infrared	4000 to 400 cm-1 Mid Infrared	400 to 4 cm-1 Far Infrared	< 4 cm-1 Microwaves Radio Waves
←				→
High Wavenumber Higher Frequency Higher Energy Shorter Wavelength				Lower Wavenumber Lower Frequency Lower Energy Longer Wavelength

Chemical bonds of a molecule vibrate when it absorbs infrared radiation. A molecule vibrates at a specific frequency. Therefore, different molecules vibrate at different frequencies because they have different chemical structures. This is why molecules can be recognized using the Infrared Spectroscopy. [36]

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

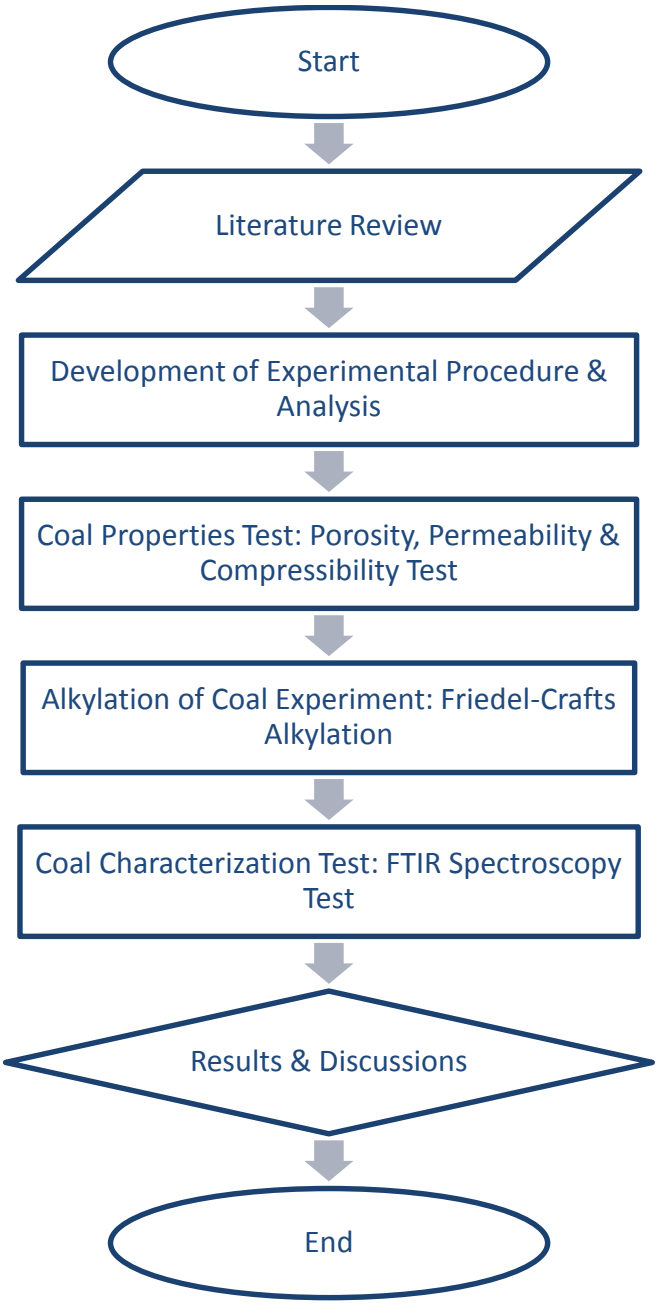


Figure 3.1: Flow chart of research methodology.

3.2 Project Activities

3.2.1 Coal Properties Test

The coal properties test is to measure the initial condition of the coal sample before the alkylation of coal is conducted. The parameters of interest for this experiment are the porosity, permeability and compressibility of the coal sample. 0.38 gram of sub-bituminous coal sample from Balingian coalfield in Sarawak is sent to the Rock Physics & Rock Mechanics Laboratory for testing. The equipment used for the test is the Mercury Porosimeter.

3.2.2 Alkylation of Coal

Friedel-Crafts alkylation process chosen for the project is based from a paper by Sharma and Mishra (1993). The experiment used carbon disulfide as the solvent, aluminum chloride as the catalyst and two types of alkylating agent, which is Butyl Bromide and Ethyl Hexyl Bromide. Two sets of experiment are conducted at the same time and a different type of alkylating agent is used in each set.

The coal is ground to 0.25 mm or 60 US mesh size and dried at 60°C for 23 hours. Then, 5 g of coal, 4 g of aluminum chloride catalyst and 100 ml of carbon disulfide solvent are treated under reflux for 24 hours. At the beginning of the reflux process, 5 ml of two alkylating agents; Butyl Bromide and Ethyl Hexyl Bromide is added dropwisely to each set over a period of 20 minutes. After 24 hours, the reaction products are cooled and acidified to pH 3 using 15% hydrochloric acid. The products are filtered and washed with methanol water (1:1 v/v) before they are dried in a vacuum oven at 80°C.

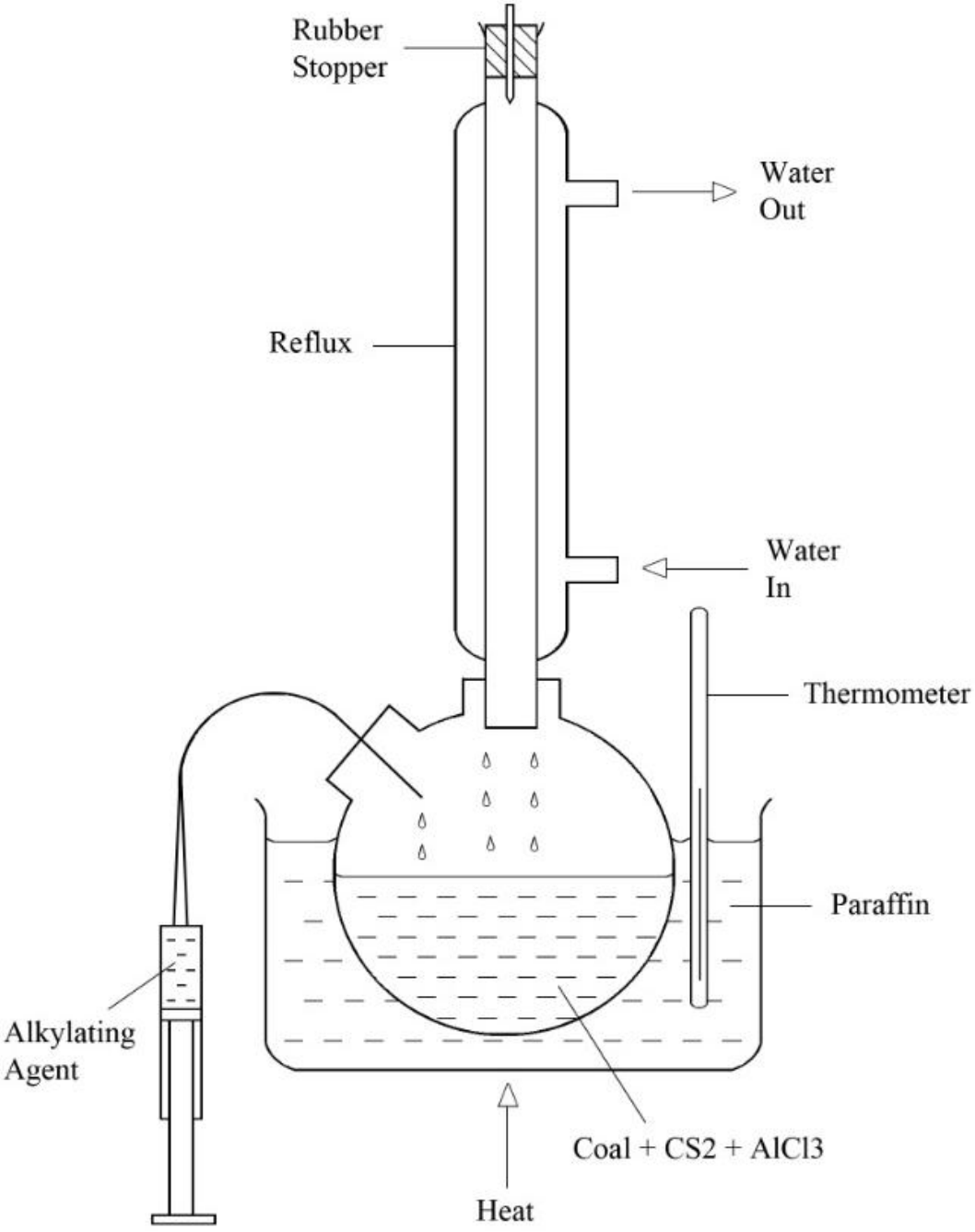


Figure 3.2: Alkylation of coal experimental setup.

3.2.3 Coal Characterization Test

This part of the project studies the effects of the alkylation process on the characterization of the coal samples. Standard coal, butyl alkylated coal and ethyl hexyl alkylated coal samples are tested to determine their characteristics using the Fourier Transform Infrared spectroscopy. This test is to verify the types of chemical bonding present in each coal samples.

3.3 Gantt Chart

3.3.1 Final Year Project 1

Table 3.1: Gantt chart of FYP 1 activities.

No.	Activity	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project topic selection														
2	Preliminary research work / consultations														
3	Submission of extended proposal														
4	Proposal defense														
5	Sample preparation														
6	Coal properties test														
7	Submission of interim draft report														
8	Submission of interim report														

3.3.2 Final Year Project 2

Table 3.2: Gantt chart of FYP 2 activities.

No.	Activity	Week																
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Coal properties test																	
2	Alkylation of coal experiment																	
3	Results and discussions																	
4	Submission of progress report																	
5	Pre-SEDEX																	
6	Submission of final draft report																	
7	Submission of technical paper																	
8	Viva																	
9	Coal characterization test																	
10	Submission of Dissertation																	

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Coal Properties Test

In this study, the porosity, permeability and compressibility of the coal sample is determined by using the mercury porosimeter. This experiment is performed before the alkylation of coal process to identify the initial properties of the coal sample. Figure 4.1, 4.2 and 4.3 shows the data collected from the experiment.

ThermoFisher SCIENTIFIC

sub-bituminous coal
Comment

Report date:02-04-14

OTHER CALC.
(Corrected curve)

RESULTS OF TORTUOSITY:

Surface area model:	Cylindrical and Plate
Tortuosity (Carniglia):	2.23
Tortuosity extended calculated:	from Tortuosity
Exponent cylindrical pore:	1.754
Tortuosity extended (Carniglia):	1.772

RESULTS OF PERMEABILITY:

Cylindrical pores permeability (µm²):	000E0
General permeability calculated:	from Tortuosity
General permeability (µm²):	170.2E-5

RESULTS OF FROST RESISTANCE:

Pore diameter 1 (µm):	0
Pore diameter 2 (µm):	0.1
Volume diff (mm³/g):	-34.478
(V/VTot) %:	-13171.167
Frost resistance value:	-27635.766

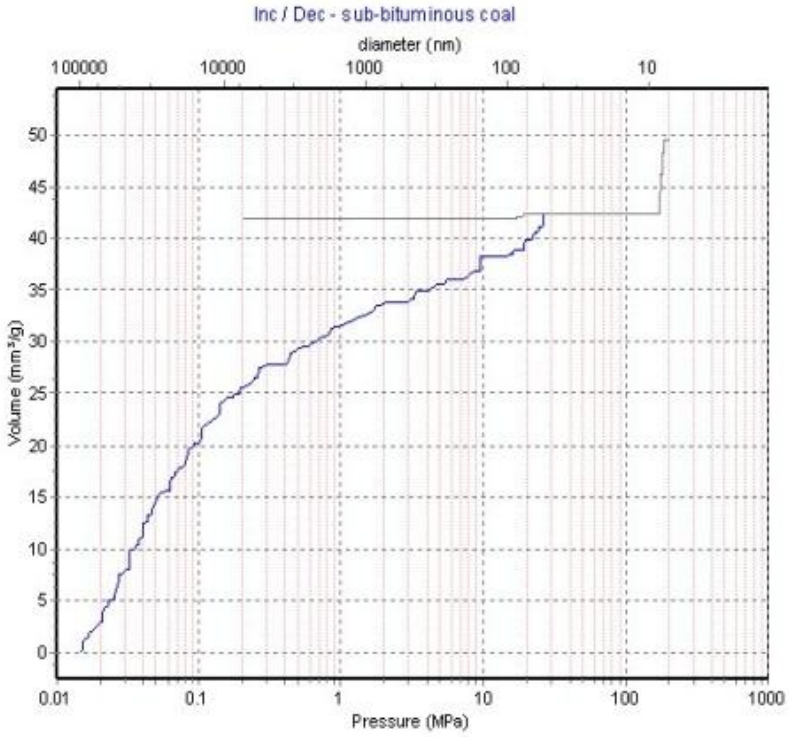
Figure 4.1: Results for permeability of the coal sample.

ThermoFisher SCIENTIFIC

sub-bituminous coal

Report date:02-04-14

SAMPLE RESULTS



RESULTS WITHOUT COMPRESSIBILITY CORRECTION

Total intruded volume (mm³/g):	49.53 at pressure of (MPa):	200.9118	
Intrud. Vol. (mm³):	10.60		
Envelope density (g/cm³):	1.2801		
Bulk density @ pressure (g/cm³):	1.3275	at pressure of (MPa):	0.367
Apparent density (g/cm³):	1.3667	at pressure of (MPa):	200.9118
Void volume by real density (mm³/g):	182.41		
Accessible porosity (%):	6.34		
Inaccessible porosity (%):	17.01		

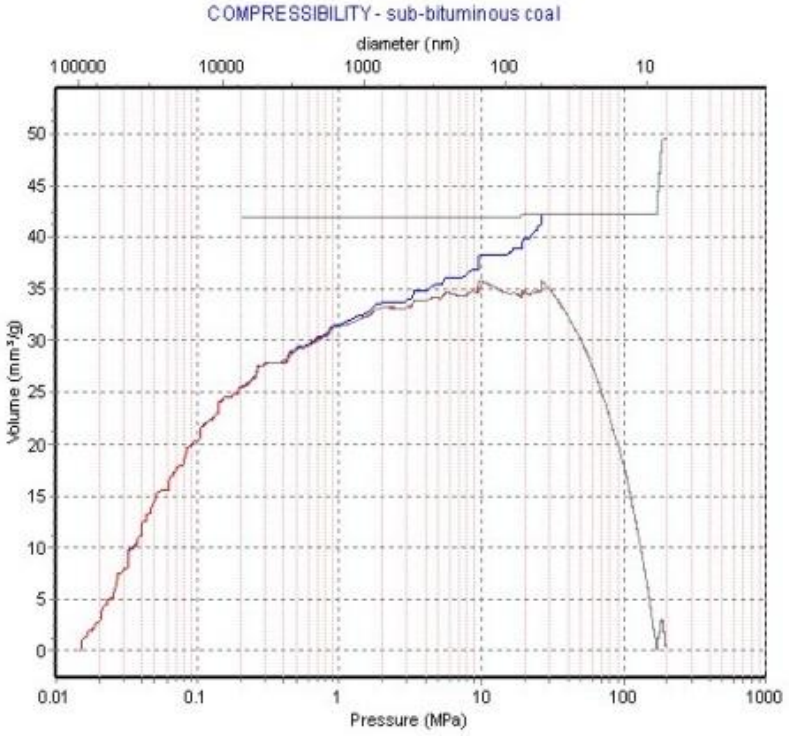
Figure 4.2: Results for porosity of the coal sample without compressibility correction.

ThermoFisher SCIENTIFIC

COMPRESSIBILITY CORRECTION

sub-bituminous coal
Comment

Report date:02-04-14



RESULTS WITH COMPRESSIBILITY CORRECTION

Correction enabled (Y/N):	Yes		
Linearity range:	From (MPa): 160.7295	To (MPa):	200.9118
Correction factor (mm³/g.MPa)	0.245223		
Compressibility factor (MPa.g/mm³)	4.0779		
Compressed volume (mm³/g):	49.27		
Sample compressibility (1/MPa):	4.951E-3		
Bulk modulus (MPa):	2.020E+2		
Total intruded volume (mm³/g):	0.26 at pressure (MPa):		200.9118
Intruded vol. (mm³):	9.42		
Envelope density (g/cm³):	1.2801		
Bulk density @ pressure (g/cm³):	1.3220	at pressure (MPa):	0.1735
Apparent density (g/cm³):	1.2805	at pressure (MPa):	200.9118
Real void volume by real dens. (mm³/g):	182.41		
Accessible porosity (%):	0.03		
Inaccessible porosity (%):	23.32		

Figure 4.3: Results for porosity of the coal sample with compressibility correction.

Figure 4.1 shows the permeability of the coal is 170.2 × 10-5 μm^2 or 1.72 mD, which is rather low. Figure 4.2 shows the total porosity of the coal sample is at 23.35 %, without compressibility correction and the accessible porosity or the effective porosity of the coal sample is 6.34 %. The coal sample has a good porosity but only small portion of the total porosity are interconnected. Whereas Figure 4.3 shows the effective porosity with compressibility correction of 0.004951 MPa^{-1} is only at 0.03 %. This means that the properties of the coal sample is not very good under high pressure conditions. Therefore, this coal sample has a poor production capability.

4.2 Alkylation of Coal

The purpose of the project is to add alkyl group to the coal sample and then study the effect of alkylating the coal on the methane adsorption. At the beginning of the experiment, during the injection of the alkylating agent into the mixture, backflow of solution is observed. It happened because of the pressure build up inside the flask as gas is produced. As a solution, the rubber stopper that sealed off the reflux apparatus is removed until the gas stop producing to prevent the flask from blowing up. This gas is identified as hydrogen sulfide due to the reaction of hydrogen that is released by the coal and sulfur from the carbon disulfide solvent. Hydrogen sulfide is a colourless gas known as sewer gas. This is the source of the rotten egg odour during the experiment. The characteristics of hydrogen sulfide are poisonous, corrosive, flammable and explosive. Therefore it is dangerous to perform this experiment at a large scale. Other type of solvent for alkylation of coal should be used to prevent the production of hydrogen sulfide gas.

Table 4.1 and 4.2 shows that the alkylation of coal experiment was run for 24 hours under a reflux just above the boiling point of the carbon disulfide solvent, which is at 46.3 °C. There is fluctuation of temperature for both coal samples because of weather conditions during the day of the experiment. Table 4.1 and 4.2 shows the recorded temperature during the alkylation of coal process using Butyl Bromide and Ethyl Hexyl Bromide as the alkylating agent.

Table 4.1: Recorded temperature during the alkylation of coal using Butyl Bromide.

Time (min)	Temperature (°C)	Time (min)	Temperature (°C)	Time (min)	Temperature (°C)
0	54	500	56	1000	56
20	54	520	56	1020	56
40	54	540	56	1040	56
60	54	560	56	1060	56
80	54	580	56	1080	56
100	55	600	56	1100	56
120	55	620	56	1120	56
140	55	640	56	1140	56
160	55	660	56	1160	56
180	55	680	56	1180	56
200	55	700	56	1200	56
220	55	720	56	1220	56
240	55	740	56	1240	56
260	55	760	56	1260	56
280	55	780	56	1280	56
300	55	800	56	1300	56
320	55	820	56	1320	56
340	55	840	56	1340	56
360	55	860	56	1360	56
380	55	880	56	1380	56
400	55	900	56	1400	56
420	55	920	56	1420	56
440	56	940	56	1440	56
460	56	960	56		
480	56	980	56		

Table 4.2: Recorded temperature during the alkylation of coal using Ethyl Hexyl Bromide.

Time (min)	Temperature (°C)	Time (min)	Temperature (°C)	Time (min)	Temperature (°C)
0	56	500	55	1000	54
20	56	520	55	1020	54
40	56	540	55	1040	54
60	53	560	55	1060	54
80	53	580	55	1080	54
100	53	600	55	1100	54
120	53	620	55	1120	54
140	54	640	55	1140	55
160	54	660	55	1160	55
180	54	680	54	1180	55
200	54	700	54	1200	55
220	54	720	54	1220	55
240	54	740	54	1240	55
260	54	760	54	1260	55
280	54	780	54	1280	55
300	54	800	54	1300	55
320	54	820	54	1320	55
340	54	840	54	1340	55
360	55	860	54	1360	55
380	55	880	54	1380	55
400	55	900	54	1400	55
420	55	920	54	1420	55
440	55	940	54	1440	55
460	55	960	54		
480	55	980	54		

After 24 hours, the two alkylated coal samples are acidified, filtered, washed with methanol water and vacuum dried. Vacuum oven is used to prevent the coal samples from burning during drying process, due to the low boiling point of carbon disulfide. Table 4.4 compares the results from two different alkylated coals produced.

Table 4.3: Comparison of the results obtained from the two alkylated coal samples.

Sample	Butyl Alkylated Coal	Ethyl Hexyl Alkylated Coal
Dry weight before alkylation	5.0163 g	5.0184 g
Dry weight after alkylation	5.7125 g	6.0994 g
Increase in weight	0.6962 g	1.0810 g
Percentage of increase	13.88 %	21.54 %

There are two alkylating agents used in the alkylation process. One is Butyl Bromide which has a straight, four carbon chain structure as shown in Figure 4.4 while the other one; Ethyl Hexyl Bromide has a branched, six carbon chain structure as shown in Figure 4.5. It is observed that, the weight of the coal samples increased after the alkylation process. This is because of precipitation formed during the experiment. Table 4.4 shows the alkylation process increases the weight of the coal sample by 21.54 % when the branched chain alkyl halide is used and only 13.88 % when a straight chain alkyl halide is used instead. Therefore, a branched and longer carbon chain of alkylating agent used for the alkylation process will have more effect on the coal. Figure 4.4 shows the structure of the straight, four carbon chain alkylating agent; Butyl Bromide and Figure 4.5 shows the structure of the branched, six carbon chain alkylating agent; Ethyl Hexyl Bromide.

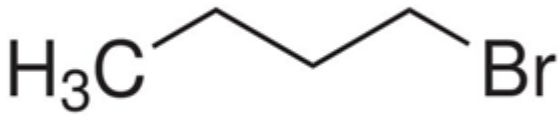


Figure 4.4: Chemical structure of Butyl Bromide. [39]

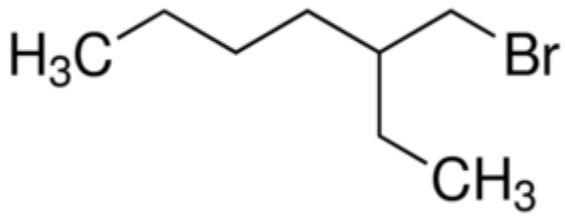


Figure 4.5: Chemical structure of Ethyl Hexyl Bromide. [40]

Figure 4.6 shows the molecular structure of coal consists of numerous stacks of benzene rings. Electron cloud is present between these stacks that act as a strong intermolecular attraction force. According to Speight (2012), alkylation process will increase the solubility of the coal. When alkyl molecule is introduced to the coal molecular structure, it act as a disturbance in the electron cloud that cause the intermolecular attraction force between the benzene rings to reduce. Therefore, the solubility of the coal increases. Figure 4.6 shows the stacking of benzene rings and the addition of alkyl group in coal structure.

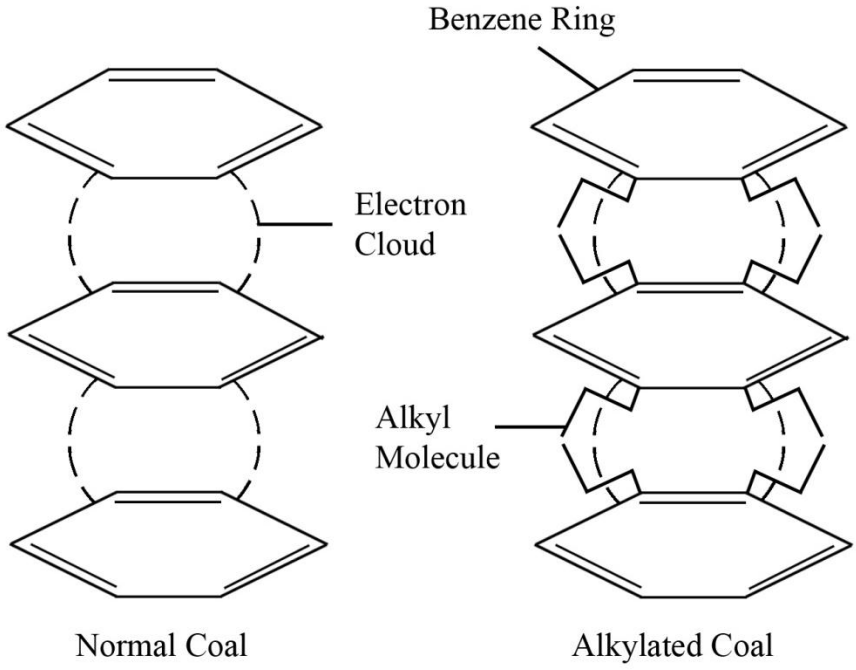


Figure 4.6: Comparison between the molecular structures of normal coal and alkylated coal.

4.3 Coal Characterization Test

In this part of the study, the standard coal, butyl alkylated coal and ethyl hexyl alkylated coal sample are characterized using the Fourier Transform Infrared spectroscopy. This test is to verify the types of chemical bonding present in each of the coal sample.

The infrared absorption spectrum which is the results of the test is divided into three regions for each coal samples to ease the results analysis process. The first region, Region A of the Infrared absorption spectrum is from 4000 cm^{-1} to 2600 cm^{-1}, Region B is from 2600 cm^{-1} to 1300 cm^{-1} and Region C is from 1300 cm^{-1} to 0 cm^{-1}. Figure 4.7 shows the infrared absorption spectrum of the standard coal sample that provides the control results for the experiment, Figure 4.8 shows the infrared absorption spectrum of the butyl alkylated coal sample and Figure 4.9 shows the infrared absorption spectrum of the ethyl hexyl alkylated coal sample.

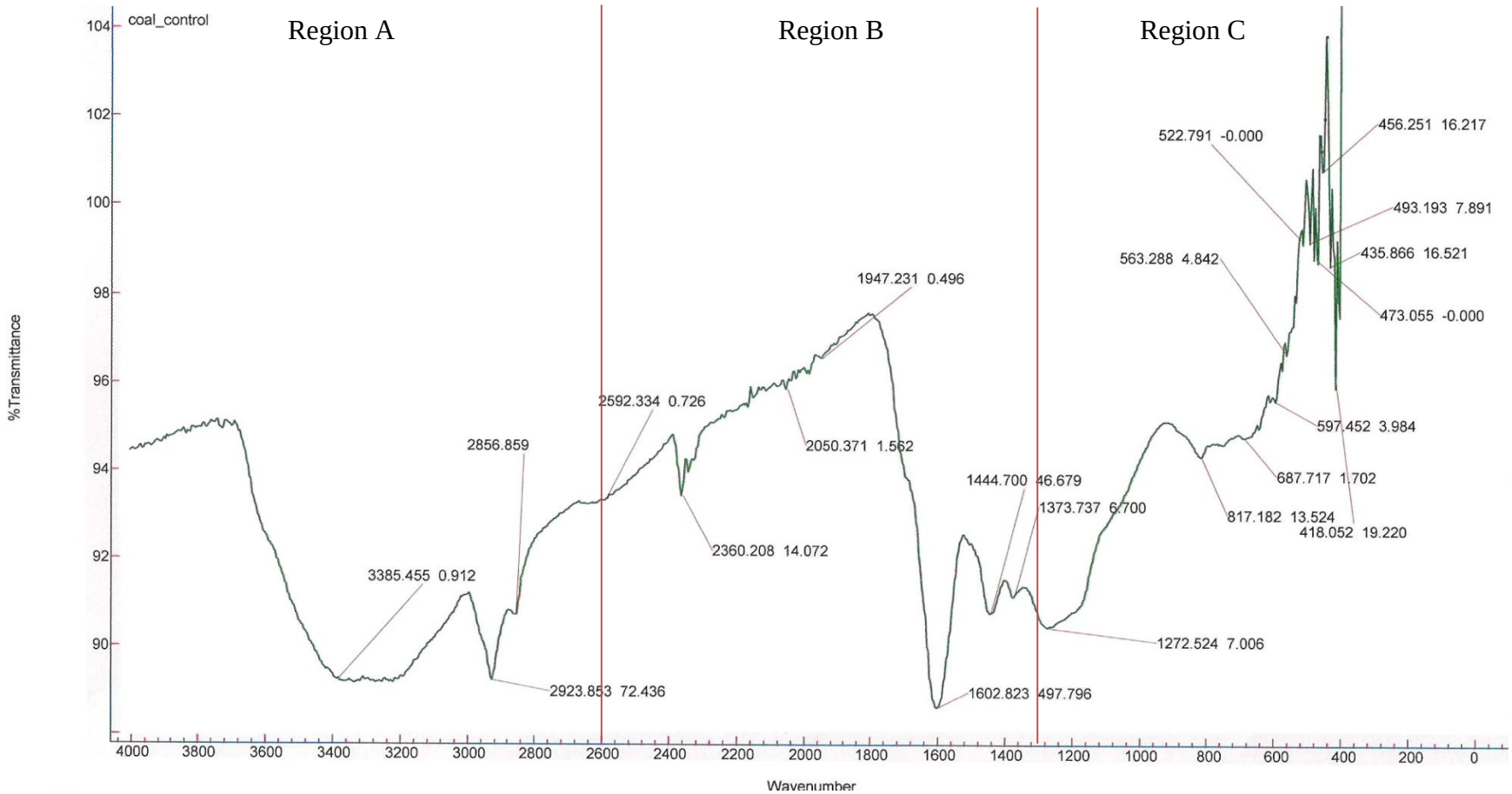


Figure 4.7: Infrared absorption spectrum of the standard coal sample.

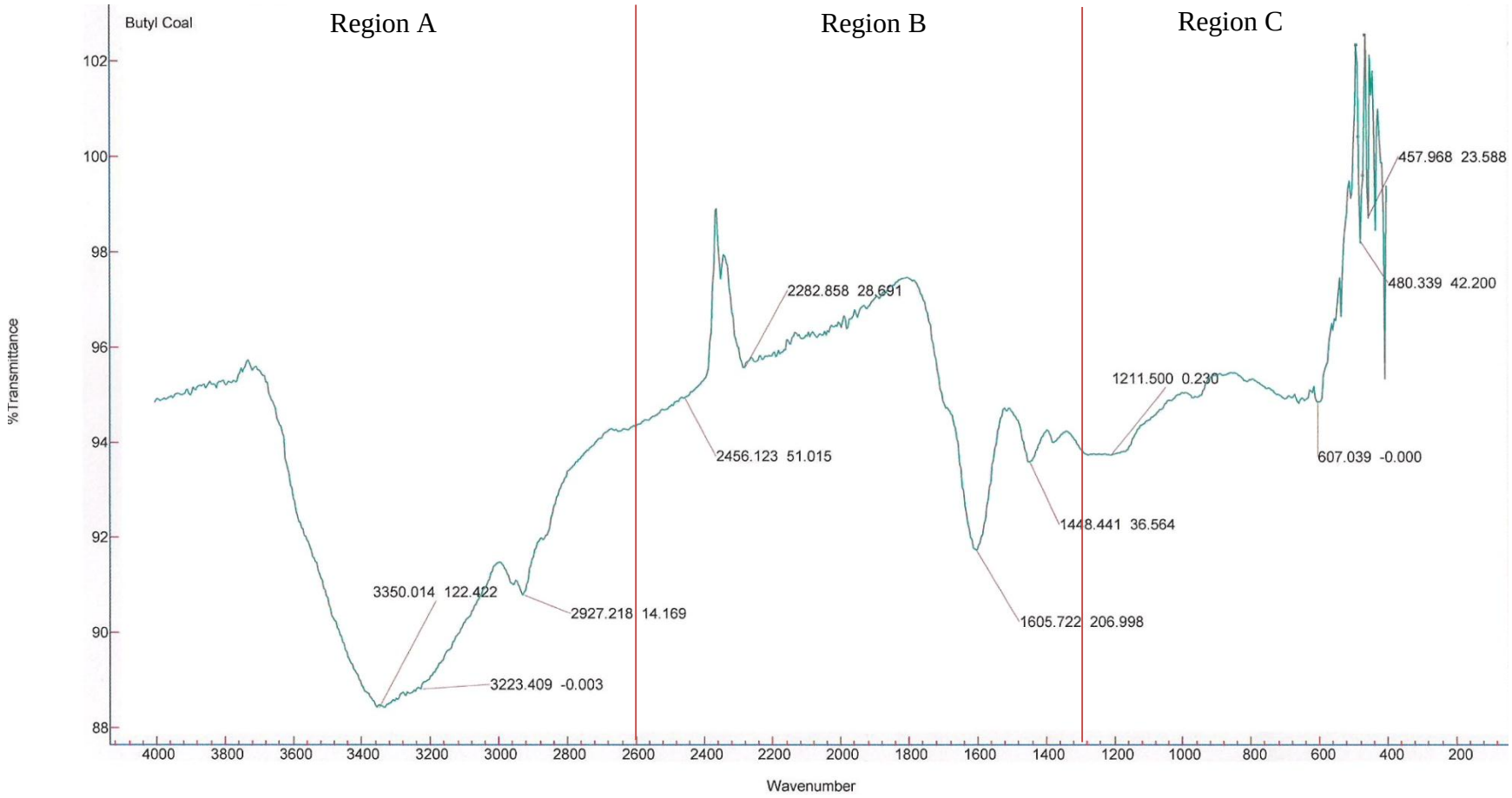


Figure 4.8: Infrared absorption spectrum of the butyl alkylated coal sample.

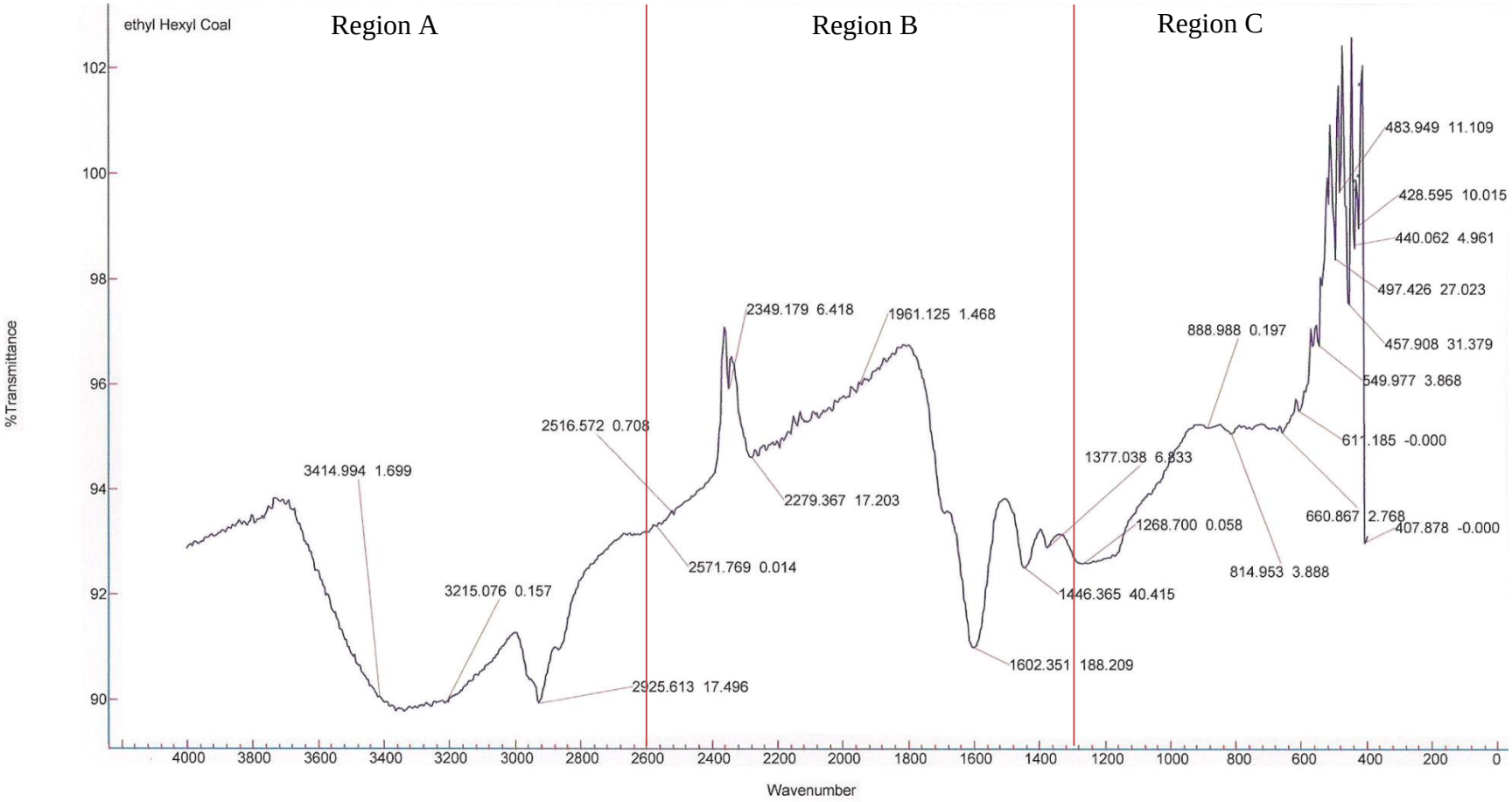


Figure 4.9: Infrared absorption spectrum of the ethyl hexyl alkylated coal sample.

Figure 4.7 shows the infrared absorption spectrum of the standard coal sample. In Region A, O-H bond is absorbs at peak 3400 cm^{-1} to 3200 cm^{-1}. There is also $=CH_2$ stretch slightly higher than 2900 cm^{-1}. In Region B, there is a peak slightly higher than 2300 cm^{-1} that indicates $=NH_2^+$ stretch and C=C aromatic at peak slightly higher than 1600 cm^{-1}. In Region C, -OH bond can be found slightly lower than 1300 cm^{-1}, C-H bond in range of 820 cm^{-1} to 680 cm^{-1} , C-Cl bond is absorbs from 600 cm^{-1} to 560 cm^{-1}, C-Br bond at peak slightly higher than 500 cm^{-1} and C-I bond at peak slightly lower than 500 cm^{-1}.

Figure 4.8 shows the infrared absorption spectrum of the butyl alkylated coal sample. In Region A, O-H bonds can be found in range of 3400 cm^{-1} to 3200 cm^{-1} and there is $=CH_2$ stretch slightly higher than 2900 cm^{-1}. In region B, there is an upward peak around 2300 cm^{-1} but unfortunately, there is no reading for the absorption that occurred at that peak. $=NH_2^+$ stretch is absorbs slightly lower than 2200 cm^{-1} and there is C=C aromatic at peak slightly higher than 1600 cm^{-1}. In Region C, there is a peak slightly higher than 1210 cm^{-1} that indicates C-F bond and C-Cl bond at peak slightly higher than 600 cm^{-1}.

Figure 4.9 shows the infrared absorption spectrum of the ethyl hexyl alkylated coal sample. In Region A, there are O-H bonds at 3400 cm^{-1} to 3200 cm^{-1} peak and there is also $=CH_2$ stretch at peak slightly higher than 2900 cm^{-1}. In Region B, =NH2+ stretch can be found from 2600 cm^{-1} to 2200 cm^{-1}. CO_2 is absorbs at the upward peak around 2300 cm^{-1} and C=C aromatic at peak slightly higher than 1600 cm^{-1}. In Region C, there are =C-H bending from 880 cm^{-1} to 820 cm^{-1}, C-Cl bond from 660 cm^{-1} to 610 cm^{-1}, C-Br bond at peak slightly below 550 cm^{-1} and C-I bond at peak slightly below 500 cm^{-1}.

Overall, it is observed that;

In Region A, the O-H bond is found from 3400 cm^{-1} to 3200 cm^{-1} for all three samples and it is absorbs differently depending on its surrounding. The butyl alkylated coal sample has a narrower O-H bond peak compare to the other two samples and it also has a shorter $=CH_2$ stretch peak slightly higher than 2900 cm^{-1}.

In Region B, C=C aromatic can be found slightly higher than 1600 cm^{-1} for all three coal samples. This shows that a coal has aromatic molecular structure which mostly is benzene ring. For the standard coal sample, there is a peak slightly higher than 2300 cm^{-1} that indicates $=NH_2^+$ stretch but for both of the coal samples that undergone the alkylation process, there is an upward peak around 2300 cm^{-1}.

The range in Region C which from 1300 cm^{-1} to 900 cm^{-1} is called the fingerprint region. This region has many small peaks that indicate the C-H rock. This region has a complex absorption pattern and it is difficult to interpret. However, each compound has its own unique pattern. Therefore, no two compounds can have the same pattern.

The infrared absorption spectrum helps to verify the types of bond present in a molecules. However, it does not tell us whether the alkylation process has any effects on the coal because a normal coal already has alkyl, O-H, C=C and C-H bond in its structure. This is why there is not very much different between each of the infrared absorption spectrum of the coal samples. In conclusion, the branched and longer carbon chain alkylating agent used during the alkylation of coal has more effects on the infrared absorption spectrum as it gave more peaks compare to the straight and shorter carbon chain alkylating agent.

CHAPTER 5

CONCLUSIONS

From this project, the effects of alkylation process on the characterization of Malaysian coal are identified. It is confirmed that, using a branched and longer carbon chain alkylating agent for the alkylation of coal will have significant effects on the coal compare to a straight and shorter carbon chain alkylating agent because the longer carbon chain alkylating agent has higher physical and chemical properties and also they are more stable than the shorter carbon chain alkylating agent.

Recommendations

Below are some recommendations for future work of this project.

- Coal Properties Test
    1. Use other equipment to measure porosity, permeability and compressibility of the coal sample so that the average coal properties data can be obtained.
    2. Use larger sample size to get better result.

- Alkylation of Coal
    1. Use different solvent and alkylating agent to get the relationship between each component of alkylation process and the methane adsorption of the coal sample.
    2. Use different solvent to avoid the production of harmful products.

- Coal Characterization Test
    1. Perform the elemental analysis test to determine how much the coal sample has been alkylated.

REFERENCES

[1] Characteristics of Coalbed Methane Production and Associated Hydraulic Fracturing Practices. (2004). Retrieved February 5, 2014, at 10.40 am, from http://www.epa.gov/ogwdw/uic/pdfs/cbmstudy_attach_uic_ch03_cbm_practices.pdf

[2] Jadhav, M. V., "Enhanced Coalbed Methane Recovery Using Microorganisms," in 15th SPE Middle East Oil & Gas Show and Conference, Bahrain, 2007.

[3] Rogers, R., Ramurthy, K., Rovelt, G., and Mullen, M. 2007. Coal Bed Methane: Principles & Practices, (3), Oktibbeha Publishing CO. LLC.

[4] Veil, J. A., Puder, M. G., Elcock, D. and Redweik, R. J. (2004). A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. Retrieved February 5, 2014, at 11.17 am, from http://www.circleofblue.org/waternews/wpcontent/uploads/2010/08/prodwaterpaper1.pdf

[5] The Future of Natural Gas. Retreived April 15, 2014, at 9.10 pm, from http://mitei.mit.edu/system/files/Supplementary_Paper_SP_2_3_Unconventional_Technology.pdf

[6] Sturgill, C. L., "Recovery and Use of Coalbed Methane," Pittsburgh, 1979.

[7] Coal Bed Methane Water Pump. Retrieved April, 8, 2014, at 7.32 pm, from http://4.bp.blogspot.com/NxvlEld0UY8/TqCNWV19mBI/AAAAAAAALgg/u4Yc9R0mtzE/s1600/CoalBedMethaneWaterPump.jpg

[8] Fulton, P. F., Parente, C. A., Rogers, B. A., Shah, N., and Reznik, A. A., "A Laboratory Investigation of Enhanced Recovery of Methane from Coal by Carbon Dioxide Injection," in SPE/DOE Symposium, Pittsburgh, 1980.

[9] Puri, R. and Yee, D., "Enhanced Coalbed Methane Recovery," in 65th Technical Conference, New Orleans, 1990.

[10] Fossil Energy Study Guide: Coal. Retrieved February 15, 2014 at 3.04 pm, from http://www.fossil.energy.gov/education/energylessons/coal/Elem_Coal_Studyguide_draft1.pdf

[11] Morris, N. 2005. Coal, Black Rabbit Books.

[12] Fossil Energy Study Guide: Coal. Retrieved February 15, 2014 at 3.02 pm, from http://energy.gov/sites/prod/files/2013/04/f0/MS_Coal_Studyguide_draft1.pdf

[13] University of Kentucky. (2012, August): Classification and Rank of Coal. [Online]. Available: http://www.uky.edu/KGS/coal/coalkinds.htm

[14] Bowen, B. H. and Irwin, M. W., "Coal characteristic", West Lafayette, 2008.

[15] University of Wollongong. Rank of Coal Seam. [Online]. Retrieved March 19, 2014, at 4.17 pm, from http://eis.uow.edu.au/outburst/html/Factors/rank.html

[16] Colgate University. (2003): Composition of coal. [Online]. Available: http://f03.classes.colgate.edu/fsem037-coal/Coal/Default/composition_of_coal.htm

[17] Drzymala, J., "Moisture & ash content", 2011. Retrieved April 14, 2014, at 10.00 pm, from https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=0CB0QFjAA&url=http%3A%2F%2Fwww.minproc.pwr.wroc.pl%2Fzpkio%2Fpdf%2FFuelProcLab%2FlabFuelProc05.pdf&ei=wFERVPqEOoSwuAT33IDwBQ&usg=AFQjCNEkiJy3L0WXDzH_iW4Luu2q2OxZYw&bvm=bv.74894050,d.c2E&cad=rja

[18] Speight, J. G. 2012. The Chemistry and Technology of Coal, (3), CRC Press.

[19] McKetta, J. J. 1993. Chemical Processing Handbook, CRC Press.

[20] Buiter, P., Spijker, P. V. and Zoonen, D. V., "Advances in Alkylation". Retrieved February 10, 2014, at 11.52 am, from https://www.onepetro.org/download?id=conference-paper%2FWPC-12313

[21] Lawrence, B., Alemany, C., Handy, I. and Stock, L. M., "Coal Alkylation Reaction. The Characteristics of the Alkylation Reactions and Products". Retrieved February 6, 2014, at 9.41 am, from http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/24_1_HONOLULU_04-79_0156.pdf

[22] Sternberg, H. W., "A Second Look at the Reductive Alkylation of Coal and at the Nature of Asphaltenes". Retrieved February 5, 2014, at 10.18 pm, from http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/Volumes/Vol21-7.pdf

[23] Sternberg, H. W., Charles, L., Donne, D. and Pantages, P., "On the Solubilization of Coal via Reductive Alkylation". Retrieved February 5, 2014, at 10.15 pm, from http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/14_1_TORONTO_05-70_0087.pdf

[24] Sternberg, H. W., and Donne, D., "Solvation and Reductive Alkylation of Coal via a 'Coal Anion' Intermediate". Retrieved February 5, 2014 at 10.17 pm, from http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/12_4_ATLANTIC%20CITY_09-68_0013.pdf

[25] Hunt, I. Friedel-Crafts Alkylation of Benzene [Online]. Retrieved July 7, 2014, at 10.14 am, from http://www.chem.ucalgary.ca/courses/350/Carey5th/Ch12/ch12-6.html

[26] Sharma, D. K., and Mishra, S., "Chemical Reactivity of Coal under Friedel-Crafts Reaction Conditions," New Delhi, 1993.

[27] Canadian Association of Petroleum Producers. Conventional & Unconventional. [Online]. Retrieved April 15, 2015, at 9.03 pm, from http://www.capp.ca/canadaIndustry/naturalGas/Conventional-Unconventional/Pages/default.aspx

[28] Northern Territory Government. (2012, September): What is the difference between Conventional and Unconventional Gas? [Online]. Available: http://www.nt.gov.au/d/Minerals_Energy/index.cfm?header=What%20is%20the%20difference%20between%20Conventional%20and%20Unconventional%20Gas?

[29] Water and Methane Production against Time. Retrieved April, 8, 2014, at 7.34 pm from http://www.intechopen.com/source/html/44208/media/image1.jpeg

[30] Xamplified. (2010): Adsorption Isotherm. [Online]. Available: http://www.chemistrylearning.com/adsorption-isotherm/

[31] Sumner, M. E. 1999. Handbook of Soil Science, CRC Press.

[32] Separation Process. Gas-Phase Adsorption Isotherms. [Online]. Retrieved April 15, 2014, at 8.46 am, from http://www.separationprocesses.com/Adsorption/AD_Chp01c.htm#TopPage

[33] Simpson, D., "Coal Bed Methane". Retrieved April 1, 2014, at 7.31 am, from http://www.sgtk.ch/rkuendig/dokumente/Coal_bed_methane.pdf

[34] Aminian, K., "Coal Bed Methane Fundamental Concepts". Retrieved January 29, 2014, at 2.49 pm from http://karl.nrcce.wvu.edu/regional/coalbedmethane_aminian_paper_1.pdf

[35] Sorption. (2007). Retrieved April 1, 2014, at 7.46 am, from http://www.halliburton.com/public/pe/contents/Books_and_Catalogs/web/CBM/H06263_Chap_03.pdf

[36] Chemwiki. Infrared: Interpretation. [Online]. Retrieved September 8, 2014, at 6.31 pm, from http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Infrared%3A_Interpretation

[37] Intertek. Fourier Transform Infrared Spectroscopy (FTIR) Analysis. [Online]. Retrieved September 8, 2014, at 7.19 pm, from http://www.intertek.com/analysis/ftir/

[38] Introduction to Fourier Transform Infrared Spectrometry. (2001). Retrieved September 8, 2014, at 6.37 pm, from http://mmrc.caltech.edu/FTIR/FTIRintro.pdf

[39] Loba Chemie. (2014): n-butyl bromide. [Online]. Available: http://www.lobachemie.com/alkyl-halides-02382/nBUTYL-BROMIDE-CASNO-109-65-9.aspx

[40] Sigma-Aldrich. 2-ethylhexyl bromide. [Online]. Retrieved August 12, 2014, at 10.59 pm, from http://www.sigmaaldrich.com/catalog/product/aldrich/249416?lang=en&region=MY